

Formation of Polymer Brushes

J. Wittmer¹ and A. Johner²

¹ *Dept. of Physics and Astronomy, University of Edinburgh
JCMB King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK.*

² *Institut Charles Sadron (UPR CNRS 022)
6 rue Boussingault, 67083 Strasbourg Cedex, France
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In systems such as block copolymer mesophases or physical gels formed by associating copolymers, the dynamical properties are often controlled by the extraction/association of a sticking group. We propose a description of the extraction/association process of a single sticker. The statistical physics of these associated systems is usually dominated by stretched brush-like regions. A sticker has to overcome a potential barrier both to penetrate the stretched structure or to escape a favorable region built by associated stickers. Our main result is that these barriers are crossed by tension fluctuations and that the corresponding processes are thus local with a friction independent of molecular weight. When the potential barriers are high, the (very stretched) equilibrium structures are not likely to develop on reasonable time scales. Stretched model systems may also be grown *in situ* from nuclei bearing initiating groups. These, irreversibly bound structures, are also briefly discussed.

Molten block copolymers self-assemble forming various structures mainly depending on their asymmetry [1,2]. In a selective solvent, say good for A bad for B , the A -blocks are swollen by the solvent whereas the B -blocks assemble in almost solvent free domains [3]. Soluble polymers decorated with insoluble stickers form a physical gel where the temporary crosslinks are built by aggregated stickers [4]. For such a material to flow, stickers have to be extracted from aggregates. There is usually a high energy barrier E to overcome during the extraction process. In the case where the stickers are small insoluble B -blocks $E \sim \gamma N_B^{2/3}$ and a high tension τ of order $a\gamma$ with a the monomer size and γ the B /solvent surface tension is needed for non activated chain extraction. Thermally activated chain extraction (or sticker desorption) is thus an important issue. Long soluble blocks strongly interact in the vicinity of an insoluble domain and stretch to avoid each other [5]. Even in the case of associating polymers forming a physical gel, it is believed that the star like regions around small insoluble domains dominate the statistical physics of the network [6]. The extraction of a sticker belonging to a locally stretched chain is thus of rather general relevance.

In the early work, over the past decade, the random motion of the sticking group has been described as that of a point-like particle with the friction $N\zeta$ relevant for the overall motion of the chain. Here we argue that the internal modes of the chain are important and that the relevant friction is much lower, it rather corresponds to the first correlation length [7] ξ , linked to the aggregate parameters through $p\xi^{d-1} \sim S$ where p is the functionality of the aggregate and S its area [8] (for insoluble blocks $S \sim (pN_B)^{2/3}$). The physical argument is as follows: once the had group is off the aggregate it almost freely diffuses over the first correlation length ξ and bounces back on the aggregate many times, at distances larger than ξ , the equilibrium tension $\tau_e \sim k_b T / \xi$ drives the motion of the sticker and extraction is achieved. This is

to say that extraction is a local process independent of the overall chain length N .

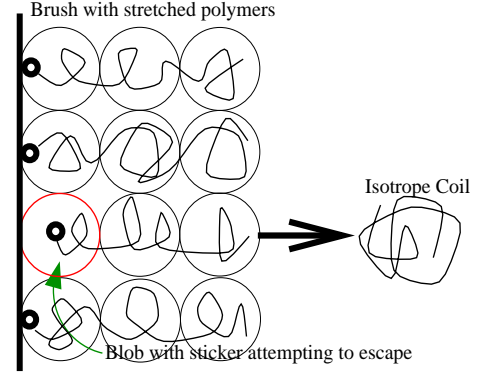


FIG. 1. Sketch of successful desorption attempt of a polymer chain out of a semi-dilute polymer brush.

The idea that the relevant friction should be local can be tested on the simpler case where a chain is cut off the grafting surface in a polymer brush (with no sticker left). Due to the retraction of the chain there is a drift of the chain end. The relevant scales are the height h of the brush and the relaxation time of the typical stretched configuration τ_r . The following scaling form must thus hold for the motion of the cut end:

$$\langle z \rangle = h f(t/\tau_r) \quad \text{with : } \tau_r \sim \left(\frac{h}{\xi} \right)^2 \xi^d \quad (1)$$

d is the dimension of space, $d = 3$ corresponds to excluded volume statistics and Rouse-Zimm dynamics whereas $d = 4$ corresponds to mean-field statistics and Rouse dynamics. Chain retraction being a local process $f(x) \sim x^{1/2}$ ($x \ll 1$) and for $t \ll \tau_r$:

$$\langle z \rangle \sim \xi \left(\frac{t}{\xi^d} \right)^{1/2} \quad (2)$$

The early motion of the chain is nonetheless dominated by anomalous diffusion: the chain end excites longer and longer modes whilst moving and the friction increases. This leads to the classical dispersion law [9]:

$$\langle (z - \langle z \rangle)^2 \rangle \sim t^{2/d} \quad (3)$$

The motion is thus driven by the tension for $\langle z \rangle \gg \xi$ (or $t > \xi^d$) when the fluctuation around the average position $\langle z \rangle$ is negligible. It is then unlikely that the chain end hits the grafting surface again. These ideas are supported by both a Monte Carlo simulation and a Rouse analysis [10].

Similar ideas hold for thermally activated had group desorption from a flat surface. Once the head group is off the grafting surface, desorption is promoted by chain retraction and becomes irreversible for $z > \xi$. The process being again local the relevant time scale depends on ξ . Assuming that at the scale of the correlation length the only time scale is the cooperative relaxation time ξ^d the outwards flux obeys:

$$J_{out} \sim \xi^{-d} \exp(-E) \sigma \sim \xi^{1-2d} \exp(-E) \quad (4)$$

and is independent of chain length, the grafting density σ is linked to ξ via $\sigma \sim \xi^{1-d}$. The characteristic lifetime of a bound sticker T_- is deduced from rate equation (4) as:

$$T_- \sim \xi^d \exp E \quad (5)$$

This also applies to curved surfaces. This result is supported by Monte Carlo simulations [10].

The inward flux J_{in} is limited by the barrier of height μ opposed to sticker penetration by already grafted chains. Assuming that the incoming sticker also crosses the barrier by a local tension fluctuation, ξ is the only relevant scale. The inwards flux thus obeys:

$$J_{in} \sim \xi^{1-d} \exp(-\mu) c_b \quad (6)$$

with c_b the bulk chain concentration. Note that the kinetic equations (4,6) correspond to the isotherm:

$$\mu_{eq} - E \sim \log(c_b/c^*) - \frac{d}{d-1} \log(\sigma/\sigma^*) \quad (7)$$

where $\sigma^* \sim R^{1-d}$ and $c^* \sim R^{-d}$ are the overlap concentrations for grafted chains and free chains respectively. The chemical potential increment μ for a grafted chain with respect to a free chain is $\mu \sim h/\xi$ to leading order, it also contains logarithmic corrections involving enhancement exponents.

Due to the activation barrier, the extraction/aggregation process is slow. The relaxation time of small fluctuations in the aggregation number (inside the peak of the size distribution) usually lies in the minute range for diblock copolymers [11,12]. Large fluctuations not conserving the number of aggregates are

in contrast found to relax extremely slowly [12]. Conversely the existence of large equilibrium aggregates is questionable. One way to overcome this difficulty is to proceed with concentrated solutions where the excluded volume is screened and to swell the system in the solvent afterwards [13]. It is however unclear how the system relaxes topological constraints upon swelling. For some purposes as colloid coating (coated colloids are used in filled rubbers) chains can be irreversibly grafted. An effective way to achieve fairly high grafting densities is to grow the layer *in situ* monomer by monomer from a functionalized nucleus carrying polymerisation initiators. We consider a flat surface densely covered with initiators. There is some similarity between needle growth [14] governed by classical D.L.A [15] without branching and polymer growth, nonetheless polymer chains can relax their configurations, this sets an additional dynamical time scale. We consider low enough growth rates such that the chain configurations are completely relaxed and the grown structure is in internal thermodynamic equilibrium at any time, this provides an additional relation between the bound monomer concentration and the density of end points.

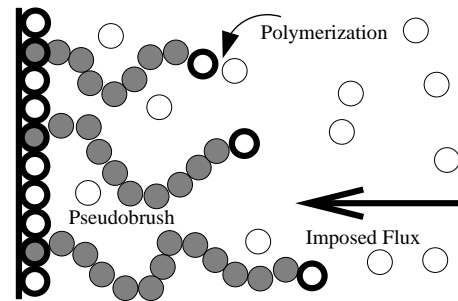


FIG. 2. Sketch of diffusive growth of a polymer layer by *in situ* polymerization

In a mean field approach, marginally valid in 3d space [16], the free monomer density u , bound monomer density ϕ and end point density ρ are determined by the following set of equations:

$$\begin{aligned} \rho &= -l \partial_z \phi^{1/\epsilon} \\ \partial_t \phi &= k u \rho \\ \partial_t \phi &= -\partial_t u + D \Delta u = D \Delta u \end{aligned} \quad (8)$$

with l a microscopic length of order the monomer size, $\epsilon = \frac{d-1/\nu}{d-1}$ an exponent linked to equilibrium properties [17,5] (ν is the Flory exponent, $\epsilon \approx 2/3$), k a kinetic constant and D the free monomer diffusion constant. The first equation expresses internal equilibrium of the layer at any time, the second describes the kinetics of the polymerisation reaction between chain ends and free monomers the third is the monomer conservation law and embodies the *adiabatic* approximation (for a discussion of this point see ref. [18]). This equations are supplemented by following boundary conditions:

$$u(0, t) = 0 \quad \lim_{z \rightarrow \infty} D \partial_z u = a^d j_\infty \quad (9)$$

The density of reacting chain ends is found to (formally) diverge at the wall and the flux of free monomers can be neglected there $\partial_z u(0, t) = 0$. We set $1/k = l = 1$ thereby choosing the time and length units, we further set $D = 1$ by an appropriate rescaling of the fields u, ρ, ϕ . The height of the structure $H(t)$ is defined by the first moment $H(t) = \int_0^\infty z \phi(z) dz / \int_0^\infty \phi(z) dz$. We now seek for a solution of the scaled form:

$$\phi = z^{-\alpha} f(x) \quad \rho = z^{-\beta} h(x) \quad u = z^\gamma g(x) \quad (10)$$

in the variable $x = z/H(t)$. The aggregation process eqs.(8,9) imposes $\beta = 2$, $\gamma = 1$ and $\alpha = \epsilon$ where the scaling function $f(x)$ is assumed to be finite at 0 and to vanish at infinity on physical grounds. The height of the brush $H(t)$ increases as a power law with time: $H(t) \sim t^{\frac{1}{1-\epsilon}}$. The scaling functions are then determined by solving eqs.(8) numerically. In fact the constitutive equation linking the monomer density ϕ and the end density ρ breaks down in the outermost correlation length, our description being coarse grained on the scale of the local correlation length we have to allow for the function $f(x)$ to jump to 0 at the brush edge. The results of this coarse grained analytical mean-field theory are nicely confirmed by Monte Carlo simulations [18]. The grown structure is densely grafted, rather polydisperse and highly stretched. It should be a good candidate for stabilisation purposes. There are early *grafting from* experiments [19] and very recent ones with a more detailed analysis of the obtained structure (mostly unpublished) [20]. The latter use thermally controlled radical precursors and the initiator formation is rate limiting, the chains are mainly grown one by one, the layers seem less densely grafted with very long, well stretched, rather monodisperse chains. There is hope that *in situ* growth allows for well stretched layers with various grafting densities, mean chain lengths, in plane structures and polydispersities controlled by the nature (anionic polymerisation has been very recently reported) and the density of the initiators (eventually by

temperature or irradiation) and by the bulk monomer concentration.

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